Density-Fluctuation-Induced Swelling of Polymer Thin Films in Carbon Dioxide

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We report an anomalous swelling of polymer thin films in carbon dioxide (CO_2) which is associated (in both locus and form) with the density fluctuation ridge that forms along the extension of the coexistence curve of gas and liquid in the P-T phase diagram. Neutron reflectivity results showed that CO_2 could be sorbed to a large extent ($\sim 60\%$) in thin polymer films even when the bulk miscibility of the polymer with CO_2 is very poor. The anomalous swelling is found to scale with the polymer radius of gyration (R_g) and extends to a distance approximately $10 R_g$.

Liquid or supercritical carbon dioxide (CO_2) are being used increasingly as a green solvent in polymer processing, polymer synthesis, reactor cleanup, and preparation of pharmaceutical products [1]. The major disadvantage thus far is that only a limited class of polymers, such as fluorinated or silicone-based polymers, can be dissolved in CO_2. Here we show that large density fluctuations in CO_2 can significantly enhance the solubility in the polymer thin films even when the bulk polymers have very poor miscibility with CO_2.

The effect of the solvent properties of CO_2 on the swelling of numerous bulk polymers has been investigated over the past two decades [2–10]. However, very little is known about the interaction of CO_2 with polymer thin films, which are of significant technological importance in coating, welding, lubrication, and adhesion. Sirard *et al.* reported that the swelling behavior of poly(dimethylsiloxane) thin films in CO_2 was different from that of the bulk polymer by using ellipsometry [11]. However, they were able to study only low pressures, up to 12 MPa, and were not able to determine the concentration profile of the polymer.

With a large penetration depth, neutron reflectivity (NR) is an ideal tool to determine the *in situ* thickness, composition, and interfacial structure of polymer thin films immersed in fluids or gases, under high pressure in thick walled vessels. On the other hand, the technical difficulties involved in delivering the neutron beams into high pressure vessels at glancing incidence have only recently been overcome by a new experimental chamber design [12]. In this Letter, we report on the first comprehensive set of *in situ* NR measurements of the swelling behavior of polymer thin films in CO_2 as a function of temperature and pressure, which allow for a direct comparison with the thermodynamic calculations of the density fluctuations. The model system we chose was a deuterated styrene-butadiene random copolymer (d-SBR, $M_w = 8.4 \times 10^4$, $M_w/M_n = 1.08$, $f_{PS} = 47\%$, Polymer Source) where deuteration would provide neutron scattering contrast. In addition, the polymer is an elastomer whose glass transition temperature $T_g = -30\,°C$, ensures that the polymer remains a liquid for all temperatures studied such that the dynamics are sufficiently rapid to reach equilibrium within the experimental time scale. The thin films were spun cast on HF etched Si substrates and were then preannealed for 5 h in a vacuum of 10^{-6} Torr at 150 °C.

High pressure experiments were performed on the NG7 neutron reflection spectrometer at NIST with a wavelength of 4.76 Å and a $\Delta\lambda/\lambda$ of 2.5%. The temperature and pressure stability of the chamber were $\pm 0.1\,°C$ and $\pm 0.2\%$, respectively. The samples were exposed to the appropriate CO_2 pressure and temperature for 30 min prior to data collection. This time was determined from shorter measurements as the interval required for the sample to reach equilibrium. The background scattering from CO_2 was also recorded simultaneously under the same conditions, since it is known from previous small-angle x-ray scattering (SAXS) studies to be a measure of the density fluctuations in the supercritical state [13]. The NR data, corrected for the background scattering, was analyzed by comparing the observed reflectivities with calculated ones based on model density profiles with three fitting parameters, film thickness, scattering length density (SLD), and interfacial roughness between polymer and CO_2 taking hyperbolic-tangent function [14]. Six

different isothermal conditions at $T = 20, 29, 32, 36, 45,$ and $50\,°C$ ($T < T_c$, $T \sim T_c$, and $T > T_c$) and two isobaric conditions at $P = 7.9$ and 10.8 MPa ($P \sim P_c$ and $P > P_c$) were investigated ($T_c = 31.1\,°C$, $P_c = 7.38$ MPa).

Representative NR data of d-SBR at $T = 36\,°C$ for three different pressures is shown in Fig. 1, where the reflected scattering intensity is plotted as a function of the momentum transfer normal to the surface, $q_z = 4\pi \sin\theta/\lambda$ where θ is the glancing angle of incidence and λ is the neutron wavelength, respectively. The solid lines are fits to the single layer profiles shown in the inset, where the values of the SLD are converted into the volume fraction of polymer in CO_2. From the inset we can see that good fits can be obtained with uniform concentrations of CO_2 into the polymer layer and no preferential adsorption of either CO_2 or polymer occurs at the Si substrate. The thickness of the layer, which is initially 385 Å thick, increases to 620 Å at $P = 8.2$ MPa and then decreases again to 423 Å upon compression up to $P = 35.0$ MPa. The interfacial roughness between polymer and CO_2 which is initially 10 Å at atmospheric pressure increases to 30 Å at 8.2 MPa and then decreases to 16 Å for 35.0 MPa. The persistence of the Kiessig fringes to large q_z values is consistent with the small interfacial roughness between the swollen films and the CO_2 layer obtained from the fits.

In Fig. 2(a) we plot the linear dilation obtained from the NR fits for the d-SBR film as a function of pressure. The linear dilation (S_f) was calculated from the equation $S_f = (L - L_0)/L_0$, where L and L_0 are the measured thicknesses of the swollen and unswollen polymer thin films, respectively. Data were obtained both by successively increasing the pressure and then slowly decreasing the pressure. The results were identical, indicating that
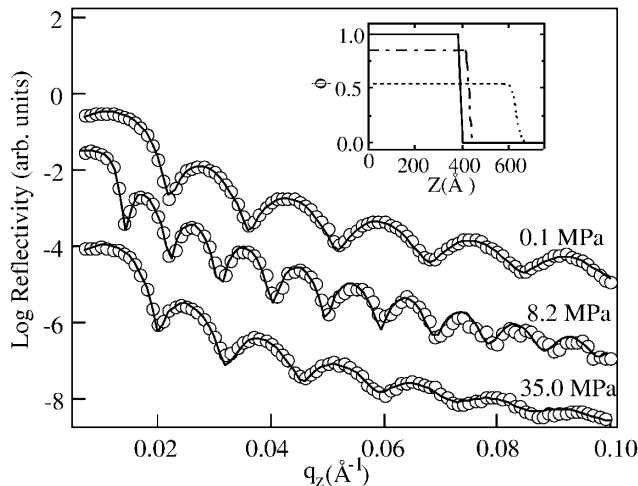
swelling isotherms of d-SBR-CO_2 mixtures were reversible. Hence the dilation was an equilibrium quantity, which was a function only of the CO_2 pressure and temperature. From the figure we can see that large maximal values of 0.6 are observed in the dilation curves at $T = 32$ and $36\,°C$ and the values of the maxima gradually decrease to approximately 0.35 with increasing temperature at $T > 45\,°C$. Small maxima, around 0.2, in dilation curves also occur for $T = 20$ and $29\,°C$ which are below T_c. As the pressure was increased well into the liquid or supercritical region, $P > 15$ MPa, the film collapses and only a small dilation of approximately 10% was observed.

Isothermal swelling of a bulk SBR sample ($M_w = 3.5 \times 10^4$, $M_w/M_n = 1.8$, $\phi_{PS} = 24\%$, 8 mm in thick, Goodyear Co.) placed in the same chamber and determined by a cathetometer are plotted (squares) in the inset 1 of Fig. 2(a) at $T = 36\,°C$. The annealing time before the measurements was set to 24 h. To compare the swelling between the thin and bulk films, we assumed that the swelling of the thin films was uniaxial [15,16] while that of the bulk (S_b) was isotropic, i.e., $S_b = [(L - L_0)/L_0]^3$. These results are similar to those reported for
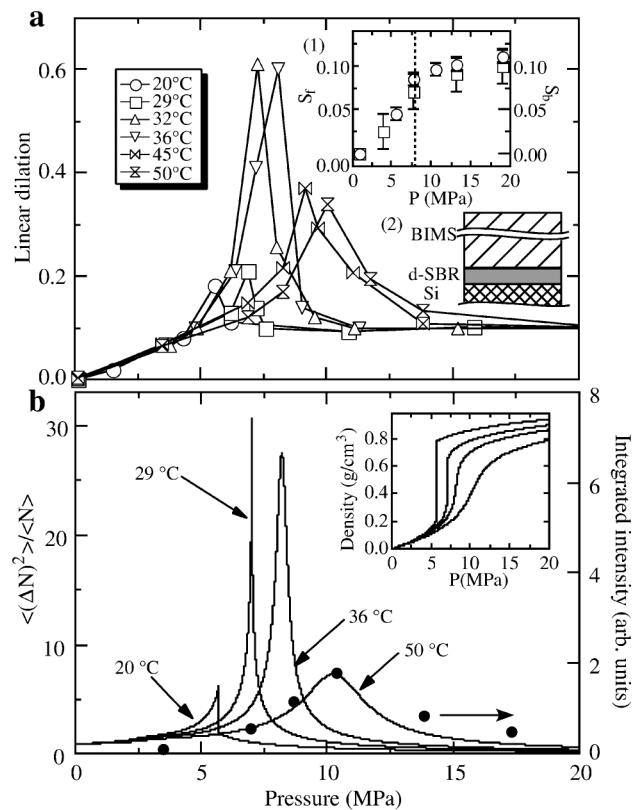

FIG. 1. Representative reflectivity data at $T = 36\,°C$. Consecutive reflectivities have been offset from each other for clarity. In the inset, d-SBR concentration profiles at $P = 0.1$ MPa (solid line), $P = 8.2$ MPa (dotted lines), and $P = 35.0$ MPa (dot-dashed lines).

FIG. 2. (a) S_f for d-SBR thin film as a function of pressure. Inset 1, S_f for d-SBR/BIMS (circles, the sample configuration is shown in inset 2) and S_b for bulk SBR (squares) at $T = 36\,°C$. (b) Calculated density fluctuations of CO_2. In the inset, calculated CO_2 density at (top to bottom) $T = 20, 29, 36,$ and $50\,°C$ are shown. Filled circles correspond to the scattering intensity from CO_2 at $T = 50\,°C$.

other polymers [2–10]. From the figure we see that the rate of dilation is maximal near the critical pressure, and a plateau, with no maxima, in the swelling at a value of 10% occurs. The bulk swelling values follow closely the increase in density of CO_2 with pressure shown in the inset of Fig. 2(b). Hence the bulk swelling is related to the monotonic increase in miscibility of the polymer with CO_2 above T_c. Since only the *rate* of miscibility, rather than the absolute value, is maximal near P_c, this does not explain the peak observed in the dilation curves of thin films.

In Fig. 2(b) we plot the data for the integrated scattering intensity from CO_2 over the q range of 0.03–0.1 Å^{-1} as a function of pressure at $T = 50\,°C$ (filled circles). Nishikawa *et al.* has shown that the scattering arising from density fluctuations in CO_2 formed the density fluctuation ridge in the P-T phase diagram [13]. This ridge, which is a general feature for the substances, is continuous across T_c and corresponds to the vapor line in the region below the critical point. Interestingly, the peak in the scattering intensity was found to identify the density fluctuation ridge reported in Ref. [13].

In order to further explore the relationship, we calculated the density fluctuations for CO_2 as a function of pressure and temperature from the thermodynamic [17]

$$\langle (\Delta N)^2 \rangle / \langle N \rangle = (N/V) \kappa_T k_B T, \qquad (1)$$

where N is the number of molecules in the corresponding volume V, k_B is the Boltzman constant and κ_T is the isothermal compressibility. In case of CO_2, the isothermal compressibility was obtained from the equation of state derived by Huang *et al.* [18]. The curves calculated for several temperatures are plotted as a function of pressure in Fig. 2(b). It is obvious that the theoretical curves can provide a good fit without any adjustable parameters to the neutron background scattering data, thereby confirming the existence of these fluctuations in our system [19].

From Fig. 2(b) one can see that the characteristic features of the ridge are (i) the amplitude of the fluctuations diverges as T_c is approached and (ii) the width of the peak is very narrow for $T \leq T_c$ and broadens with increasing temperature and pressure above the critical point. Comparing the S_f data in Fig. 2(a) with the theoretical calculations in Fig. 2(b), we find that the position and the width of the peaks in the lateral dilation curve exactly coincide with those in the calculated curves for $T > T_c$. This then suggests that the anomalous dilation observed is correlated to the density fluctuations in CO_2. The only exception occurs at $T = 29\,°C$, where the maximum in the S_f curve is seen to be relatively much smaller than the calculated value. This is probably due to the fact that, as can be seen in Fig. 2(b), for $T < T_c$ the expected peak is much narrower than the experimental resolution of both temperature and pressure.

This effect was further investigated by observing the S_f curves of the d-SBR films under two isobaric conditions at $P = 7.9$ and 10.8 MPa. In the case of the isobaric experiments, one crosses into the supercritical region from the liquid, rather than the gas phase, where the density fluctuation ridge is much deeper into the supercritical regime. In Fig. 3 we plot the temperature dependence of S_f together with the calculated curves for the normalized amplitudes of the density fluctuations. From the figure we can see that, as in the case of the isothermal curves, our data can be superimposed on the calculated curves. Hence we find that the anomalous dilation is not simply induced by the supercritical state. Rather it appears to be an equilibrium phenomenon, which is associated with only $\langle (\Delta N)^2 \rangle / \langle N \rangle$, and is independent of the direction of approach to the ridge [20]. Thus, we can conclude that the long-range density fluctuations can directly control the absolute solubility of CO_2 in the polymer thin films while the solubility of the bulk is correlated to the density-dependent solubility of CO_2.

In order to further explore whether the dilation is an artifact of anomalous adsorption to the polymer/substrate interface, we simulated bulk conditions around the thin films by pressing a 1 mm thick disk of brominated poly(isobutylene-co-p-methylstyrene) (BIMS) directly onto the d-SBR layer (inset 2 of Fig. 2(a)). The results are plotted as circles in the inset 1 of Fig. 2(a). Here we see that the measured S_f values of the thin film directly overlaps that measured for the bulk sample. Hence we conclude that the dilation we have observed may be strictly limited to the interfacial region between the polymer and CO_2 layers, and is easily observable only in thin
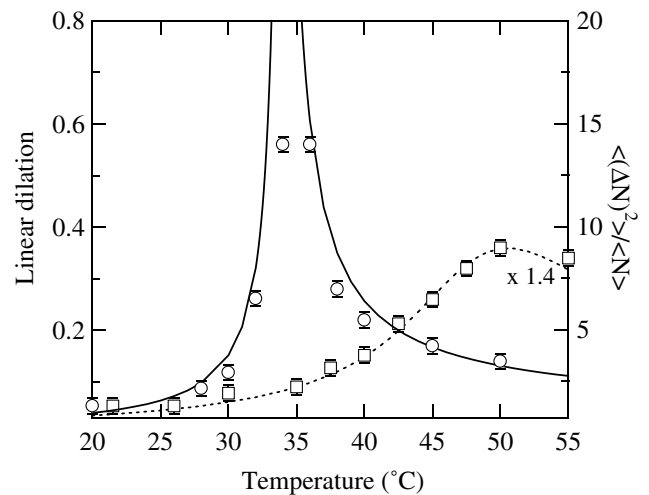

FIG. 3. Temperature dependence of S_f for d-SBR thin film at $P = 7.9$ MPa ($\bigcirc$) and 10.8 MPa ($\square$) and $\langle (\Delta N)^2 \rangle / \langle N \rangle$ at $P = 7.9$ MPa (solid line) and 10.8 MPa (dotted line). As of the qualitative comparison, the $\langle (\Delta N)^2 \rangle / \langle N \rangle$ values at $P = 10.8$ MPa were multiplied by 1.4, which is arbitrary at the moment since we do not as yet have a quantitative theory relating the absolute magnitude of the two amplitudes.
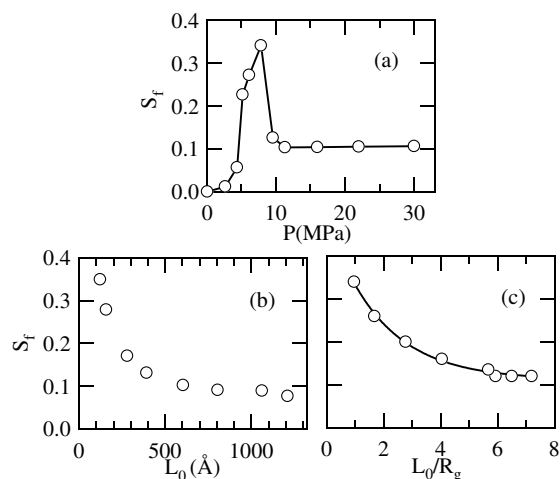
FIG. 4. (a) S_f for d-PS thin film at $T = 36\,°C$. (b) S_f for d-PS vs film thickness at $T = 36\,°C$ and $P = 8.2$ MPa. (c) Scaled thickness dependence of S_f for d-PS thin films at $T = 36\,°C$ and $P = 8.2$ MPa. Swelling behavior is well described by the exponential function shown by the solid line, $S_f(T = 36\,°C, P = 8.2 \text{ MPa}) = 0.11 + 0.37 \exp(-0.53 L_0/R_g)$.

films or at interfaces. In the case of very thick films, only the surface region is affected. Since this region is a small part of a bulk sample, it is difficult to detect in bulk measurements.

Finally, we shall discuss the penetration depth of the swelling. For this purpose, we chose thin deuterated polystyrene (d-PS) films, since it also has poor miscibility with CO_2 in the bulk, but unlike d-SBR, a wide range of monodisperse deuterated polymers are commercially available. All d-PS polymers were obtained from Polymer Laboratories, and the polydispersity indices, M_w/M_n, were 1.1 or less. In Fig. 4(a) S_f for d-PS film ($M_w = 15.5 \times 10^4$) with 130 Å thickness is plotted as a function of pressure at $T = 36\,°C$. Here again we see the dilation peaks of 0.34 at the ridge, which is much larger than the bulk value of 0.07 [12]. As we increased the film thickness, the maximum S_f value at the ridge decreased to the bulk value at a thickness of ~ 1200 Å (the maximum thickness resolved by NR) (Fig. 4(b)). Similar experiments were performed at the ridge ($T = 36\,°C$ and $P = 8.2$ MPa) with L_0 varying from 300 to 1250 Å and M_w varying from 9.4×10^4 to 195×10^4. The results for the different thicknesses and molecular weights are plotted in Fig. 4(c), where we see that the data collapse onto one curve when they are scaled by R_g [$= 6.7$ Å $\times (N/6)^{1/2}$] where N is the polymerization index. From the figure we therefore conclude that the anomalous dilation is a surface effect which occurs only within $\sim 10 R_g$ of the polymer/CO_2 interface [21].

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[19] In case of CO_2, most of the scattering intensity arises from the correlation length of 10–20 Å [13] so that the integrated and calculated points are still in good agreement.
[20] Note that S_f for $T = 34$ and $36\,°C$ is similar even though the amplitude of $\langle (\Delta N)^2 \rangle / \langle N \rangle$ is already decreased at $T = 36\,°C$. This may be due to the fact that the degree of chain stretching reflects the balance between a loss of entropy and a gain in enthalpy.
[21] To simplify the neutron fitting procedure we assumed a homogenous density in the films. This approximation is clearly not correct for the thicker film, but due to the small q range available with neutrons, could not be investigated further *in situ*. In a forthcoming publication we will describe the results obtained with x-ray reflectivity on rapidly quenched samples where the density gradient is accurately mapped.